

**Appendix A. Supplementary material**

# A fluorescence turn-off-on chemosensor based on carbon nanocages for detection of ascorbic acid

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## **S1. Supporting experimental methods**

### ***S1.1 Fluorescence quantum yield and lifetime measurement***

The quantum yield ( $\Phi$ ) of CNCs was estimated by comparing the integrated fluorescence intensities and the absorbance values against the quinine sulfate standard and it was calculated using Eq. (1). Quinine sulfate with quantum yield ( $\Phi_r$ ) = 0.54 was dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub> (refractive index ( $\eta_r$ ): 1.2), and the CNCs were dissolved in deionized water (refractive index ( $\eta$ ): 1.2).

$$\Phi = \Phi_r \frac{I A_r \eta^2}{I_r A \eta_r^2} \quad (1)$$

Here  $\Phi$  is the quantum yield,  $I$  is the measured integrated emission intensity,  $\eta$  is the refractive index, and  $A$  is the optical density. The subscript r represents the reference fluorophore of known quantum yield. Absorbance values of each solution in cuvette were maintained under 0.1 at the excitation wavelength to minimize reabsorption effects. Excitation and emission slit widths were both 4.5 nm for the fluorescence spectra measurement. The fluorescence lifetime ( $\tau$ ) of the CNCs was calculated using Eq. (2).

$$R(\tau) = B_l e^{-\tau/\tau_l} \quad (2)$$

Herein  $B_l$  is the fractional contributions of time-resolved decay lifetime of  $\tau_l$ .

### ***S1.2 FT-IR***

FTIR spectra were obtained from discs containing 2 mg of CNC sample in approximately 100 mg potassium bromide (KBr). To ensure acceptable signal-to-noise ratio, each spectrum was obtained by 16 scans at 4 cm<sup>-1</sup> resolution. Fourier self-

deconvolution (FSD) was performed between 4000 and 400  $\text{cm}^{-1}$ . Triplicate samples of CNCs were analysed.

### ***S1.3 UV spectroscopy***

The samples were prepared by dissolution in ultrapure deionized water with a sample/solution ratio of 1:200 (w/v). The ultraviolet absorption spectra of extracted CNCs were recorded individually by a spectrophotometer in the spectral range of 200–700 nm with a slit width of 5 nm.

### ***S1.4 pH and Time dependent stability study of CNCs***

To estimate the pH stability of CNCs, CNCs were dissolved in B-R buffer with different pH from 2.0~11.0 at the concentration of 5 mg/ml. After a thoroughly mixing for 2 min at room temperature, the fluorescence intensity was recorded at the excitation wavelength of 330 nm and emission wavelength of 390 nm. Then a solution of CNCs (5 mg/ml) was prepared in B-R buffer (pH 7.0). The stability of CNCs was assessed by monitoring the fluorescence intensity at 0, 2, 4, 8, 12, 18, 24, 36, 48 h with the excitation wavelength of 330 nm and emission wavelength of 390 nm.

### ***S1.5 pH and Time dependent stability study of CNCs-Fe<sup>3+</sup>***

Both of pH and time dependent stability are important factors for CNCs-Fe<sup>3+</sup> probe. To estimate the pH stability of CNCs-Fe<sup>3+</sup>, CNCs and Fe<sup>3+</sup> were dissolved in B-R buffer (pH 2.0~11.0) with the concentration of 5 mg/ml and 100  $\mu\text{M}$ . After equilibrating 5min, the fluorescence intensity was recorded using a 330 nm excitation wavelength and 390 nm emission wavelength.  $F_0$  is the CNCs fluorescence intensity before addition of Fe<sup>3+</sup> ions.  $F_1$  is the CNCs fluorescence intensity after addition of

metal ions. The quenching efficiency  $(F_0-F_1)/F_0$  was calculated.

Then time stability was investigated, CNCs and  $Fe^{3+}$  were dissolved in B-R buffer (pH 8.0) with the concentration of 5 mg/ml and 100  $\mu$ M. After different reaction time, such as 2, 4, 6, 8, 10, 12, 14, 16, 18, 20min, measuring the fluorescence, the quenching efficiency  $(F_0-F_1)/F_0$  was calculated by the same method of pH stability study of CNCs- $Fe^{3+}$ .

### ***S1.6 Selectivity study of CNCs “turn-off” by $Fe^{3+}$***

All the metal salts of  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$  and  $Fe^{2+}$  were dissolved in B-R buffer (pH 8.0) to prepare the stock solution with the concentration of 220  $\mu$ M. CNCs also were dissolved in B-R buffer (pH 8.0) to give the stock solution (10 mg/ml). After mixing two kinds of stock solution( $v/v=1:1$ ) to get the final concentration of 110  $\mu$ M metal cations and 5mg/ml CNCs, and standing for 30 minutes, the fluorescence intensity was recorded at 330 nm excitation wavelength and 390 nm emission wavelength.  $F_0$  is the CNCs fluorescence intensity before addition of metal cations.  $F_1$  is the CNCs fluorescence intensity after addition of metal ions. Then, the quenching efficiency  $(F_0-F_1)/F_0$  was calculated.

### ***S1.7 pH and Time dependent stability study of CNCs- $Fe^{3+}$ -AA***

To achieve high sensitivity and precision, the detection conditions including pH values and interaction time were optimized. 5 mg/ml CNCs were quenched by 100  $\mu$ M  $Fe^{3+}$  to get the CNCs- $Fe^{3+}$  probe system in B-R buffer (pH 2.0~11.0). Then AA was also added in different pH CNCs- $Fe^{3+}$  probe system with the final concentration of 10  $\mu$ M. After equilibration for 10 min at room temperature,  $F_1$ ( the probe fluorescence

intensity before addition of AA) and  $F_2$  (probe fluorescence intensity after the addition of AA) were recorded with a fluorescence spectrometer using an excitation wavelength of 330 nm and emission wavelength of 390 nm, then the fluorescence restoration  $F_2/F_1$  was calculated. Moreover, time stability was investigated, 5 mg/ml CNCs were quenched by 100  $\mu\text{M}$   $\text{Fe}^{3+}$  in B-R buffer (pH 7.0), then added AA with the final concentration of 10  $\mu\text{M}$ . After different reaction time, such as 2, 4, 6, 8, 10, 12, 14, 16, 18, 20min, measuring the fluorescence, the fluorescence restoration  $F_2/F_1$  was calculated by the same method of pH stability study of CNCs- $\text{Fe}^{3+}$ . The control groups were assessed without  $\text{Fe}^{3+}$ , and pH and time dependent stability studies were evaluated by similar methods as CNCs- $\text{Fe}^{3+}$ -AA.

### ***S1.8 Selectivity study of CNCs- $\text{Fe}^{3+}$ “turn-off” by AA***

In the selectivity measurements of AA, several co-existing substances were selected, such as AA, UA, dopamine, HAS, Hb and D-glucose. The concentration of all substances was 10  $\mu\text{M}$  in the solution containing 5 mg/ml CNCs and 100  $\mu\text{M}$   $\text{Fe}^{3+}$ , and the same detection conditions were selected as mentioned in S1.6 .

### **Supporting results**

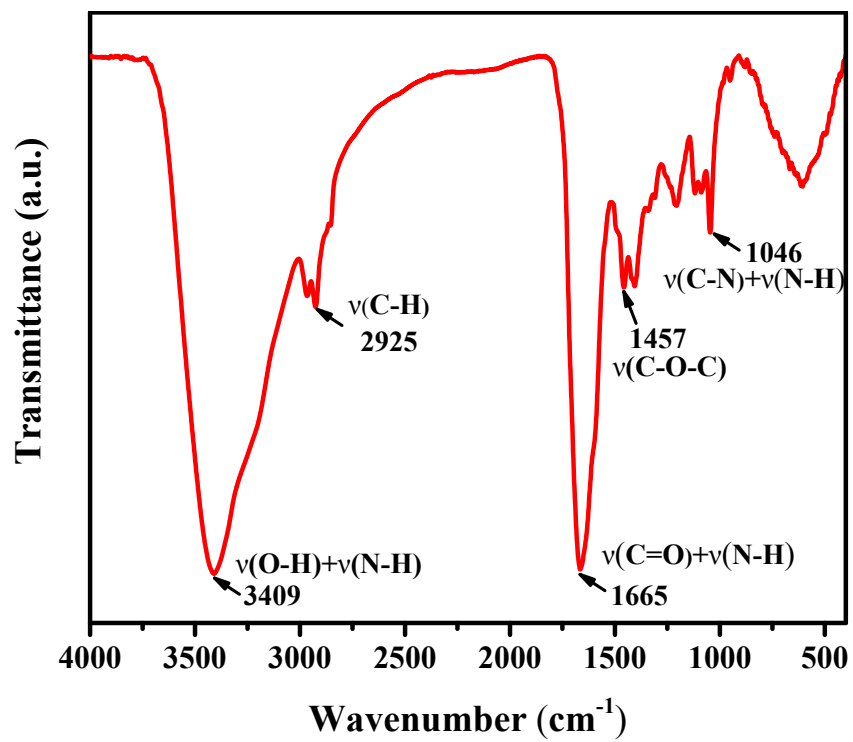


Fig. S1 FTIR spectra of CNCs from grilled turbot flesh at 230 °C for 30 min.

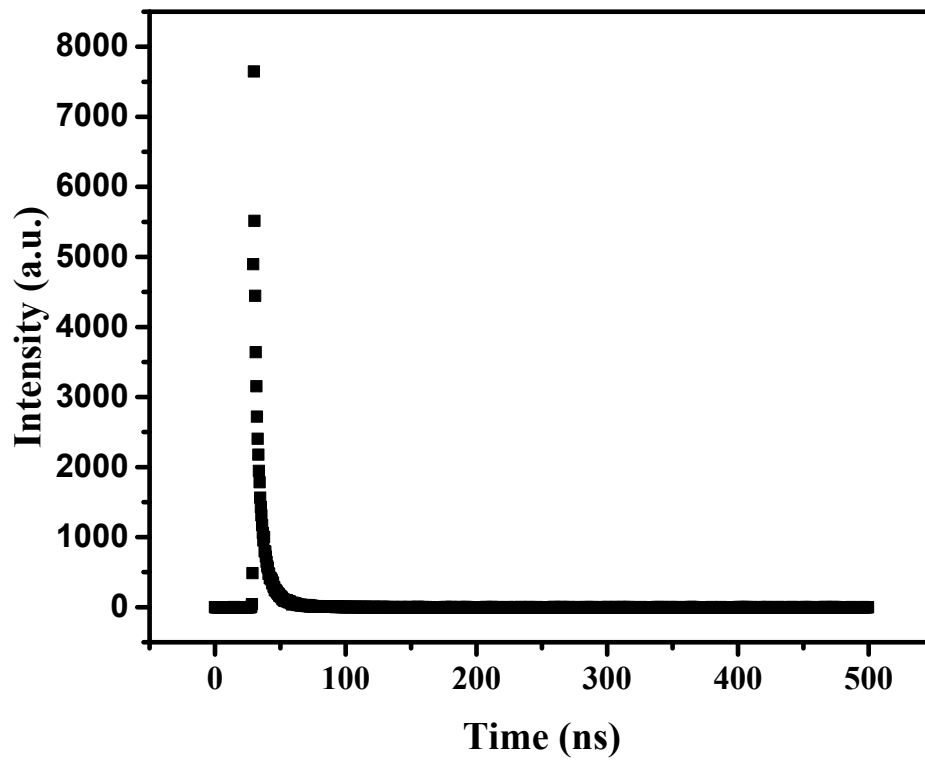


Fig. S2 Fluorescence decay curve of CNCs from grilled turbot.

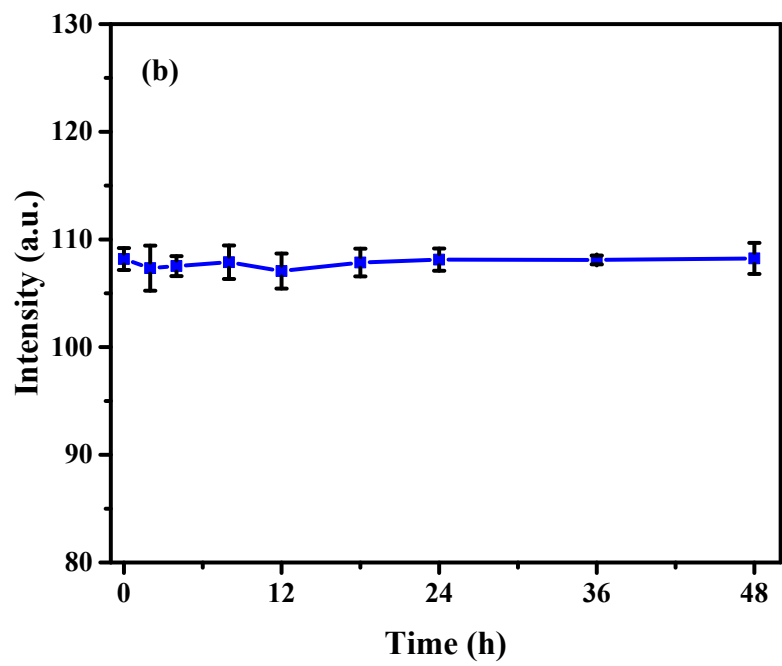
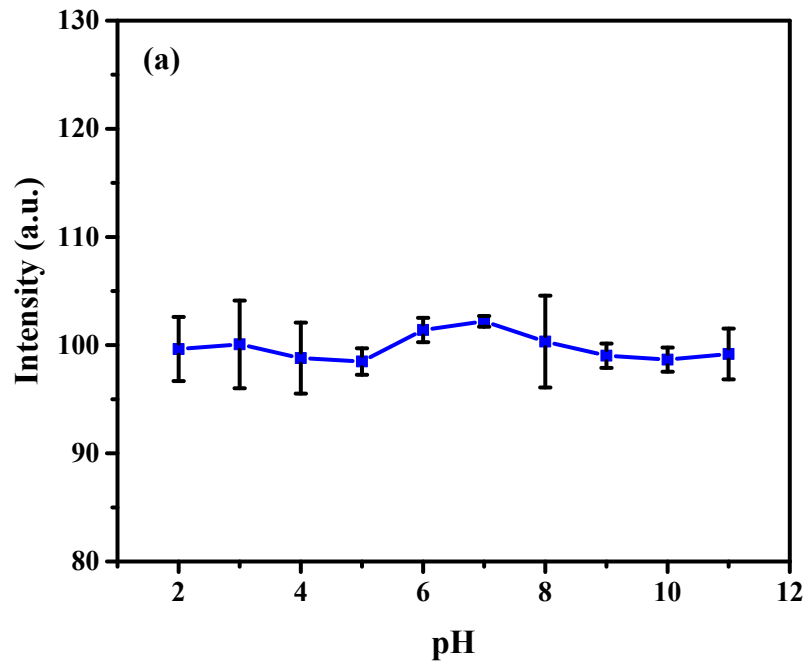


Fig. S3 (a) pH and (b) time effect on the fluorescence intensity of CNCs extracted from grilled turbot.



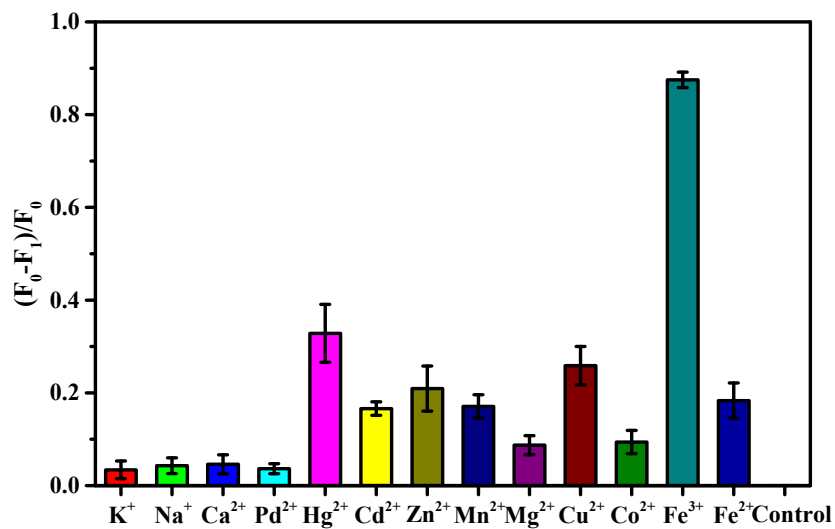


Fig. S4 Quenching efficiency  $(F_0 - F_1) / F_0$  of the CNCs dispersion under various metal ions including K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> (Metal ions concentration of 110  $\mu$ M).

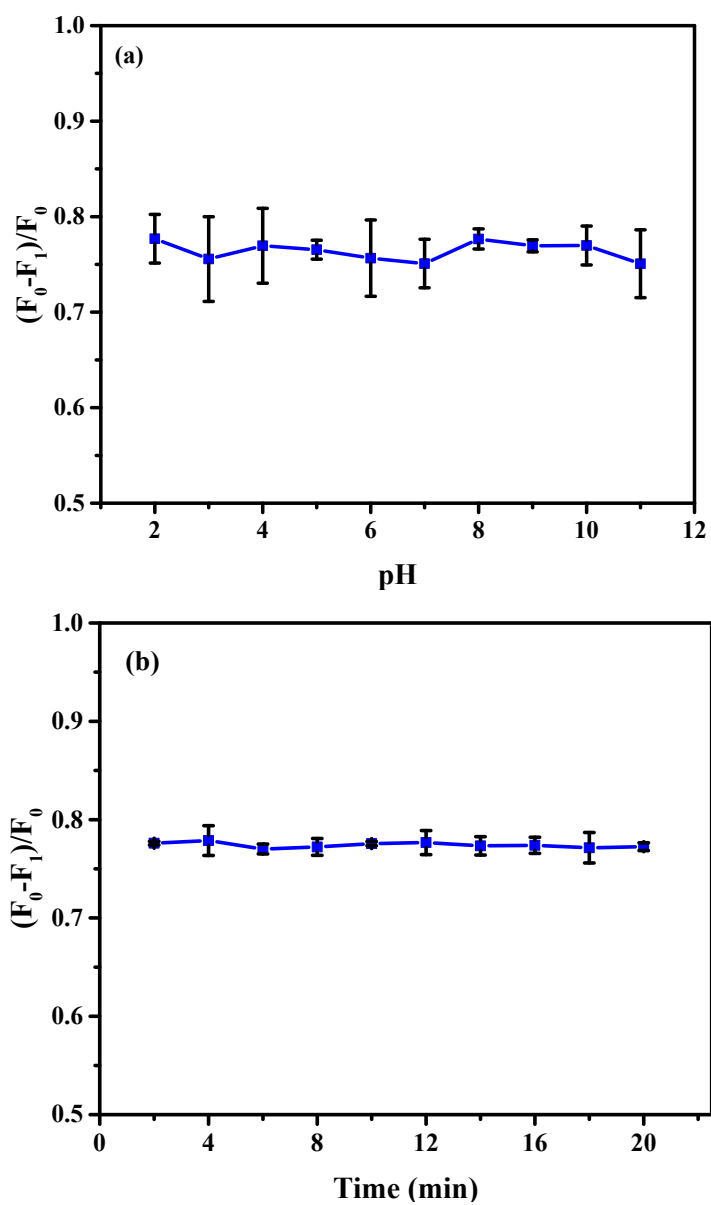


Fig. S5 (a) pH and (b) time effect on the quenching efficiency  $(F_0 - F_1)/F_0$  of CNCs-Fe<sup>3+</sup> complex.

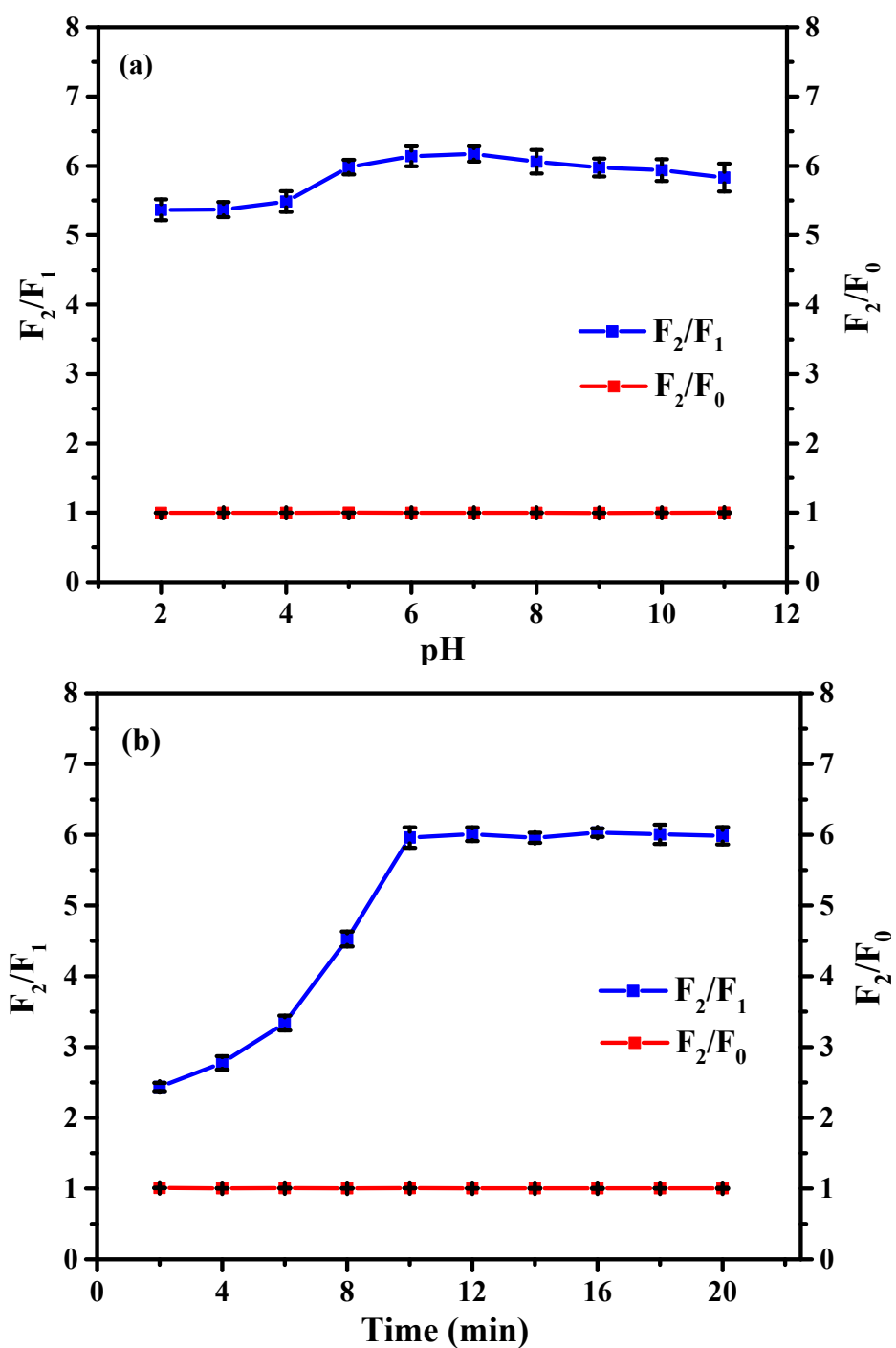


Fig. S6 (a) pH and (b) time effect on the fluorescence restoration  $F_2/F_1$  of CNCs-Fe<sup>3+</sup> by the addition of AA.  $F_1$  is the fluorescence intensity of CNCs-Fe<sup>3+</sup> before addition of AA, and  $F_2$  is the fluorescence intensity of CNCs-Fe<sup>3+</sup> after the addition of AA.  $F_0$  is the fluorescence intensity of CNCs before addition of Fe<sup>3+</sup> ions.

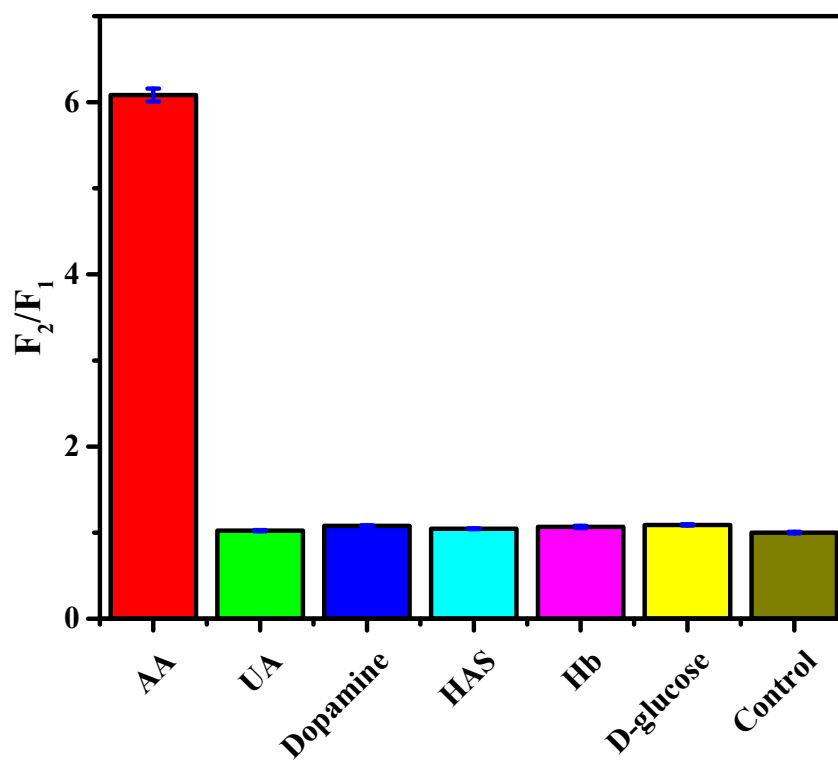


Fig. S7 The difference in the fluorescence restoration  $F_2/F_1$  of CNCs- $Fe^{3+}$  by the addition of various potentially interfering species including AA, UA, dopamine, HAS, Hb and D-glucose.